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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 19 September 2003 with an application for Letters Patent number 528353 made by KERATEC LIMITED.

Dated 1 October 2004.

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PROVISIONAL SPECIFICATION

COMPOSITE MATERIALS CONTAINING KERATIN

We, **KERATEC LIMITED,** a New Zealand company, of Corner Springs & Ellesmere Junction Roads, Lincoln, Canterbury New Zealand do hereby declare this invention to be described in the following statement:

PT043797012

COMPOSITE MATERIALS CONTAINING KERATIN

Field of the invention

This invention describes polymeric materials which contain keratin proteins as one component, in a composite, polyblend, or graft copolymer with another polymeric material, which may be of synthetic or natural origin, and formed by polymer blending or by in-situ polymer formation. These materials may be processed into fibres, or be created as part of a fibre forming process, or as materials used in other forms.

Background

Keratin fibres, such as wool and animal hair, possess many desirable properties, such as comfort and handle and have been used for thousands of years as the basis for clothing and textiles. Some of these properties can be associated with the way that the fibres interact with water both in terms of absorbing water and allowing water vapour transport, due largely to the hydrophilic nature of the proteinacous material that comprises the bulk of keratin fibres. Keratin fibres also exhibit useful specific reactivity with dyestuffs and other materials that allows a range of modifications to be undertaken on the fibres. This arises in part from the range of chemical groups present on the keratin proteins that make up the fibres.

Synthetic fibres, and the polymers from which they are derived, in many cases do not possess the same hydrophilic character and so have quite different comfort characteristics. In addition they are largely monofunctional, restricting the variety of modifications that can be performed on them. However, synthetic materials have a wide range of very desirable properties which has led to their widespread use. Included

in these desirable properties is processability, for example the ability to be thermoformed or extruded into a fibrous form, and many commercially advantageous properties arise from this. Typical properties that extruded fibres exhibit by virtue of their processability include the ability to be produced as a continuous filament, the ability to be produced with a defined cross-section and fibre diameter and the ability to include other materials within the fibre prior to extrusion, such as inexpensive or lightfast dyestuffs.

It is an object of the invention to create materials which may be fibrous or in other forms through the combination of keratin proteins with other polymeric materials to produce materials with properties arising from the particular characteristics of each component.

Summary of the invention

The broadest aspect of the invention includes materials that combine keratin with another polymer or polymer forming material to create a composite material.

Another aspect of the invention describes fibres, and processes for their production, in which keratin protein is combined with another polymer or polymer forming material.

A further aspect of the invention describes processes for creating an intimate mixture of keratin protein with another material of either natural or synthetic origin, which is formed by extruding one material into a solution of the other material.

Another aspect of the invention describes processes for creating an intimate mixture in which keratin protein and another polymer or polymer forming material are mixed and then coextruded.

An aspect of the invention describes processes for coating preformed fibres, of either natural or synthetic origin, with keratin protein, including methods to prepare the fibre surface to create a stable keratin coating.

A further aspect of the invention describes a process of graft copolymerisation in which a synthetic monomer is polymerised in the presence of keratin protein and a material is formed.

A particular aspect of the invention involves combining keratin proteins with fibre-forming polymers which may be co-extruded, as parallel combined filaments, as a polyblend, or as a graft copolymer system, to form 2-phase fibres.

Detailed description of examples of the invention

Many aspects of the invention detail the use of keratin proteins in combination with other materials. These keratin proteins can be extracted from wool or another keratin source, such as horns, hooves or feathers, by a variety of mechanisms, including the established keratin dissolution processes of reduction, oxidation, oxidative sulfitolysis, or protein hydrolysis (either chemical or enzymatic) such as that the subject of the applicants PCT/NZ02/00169.

In its broadest form the invention describes materials including fibres produced by combining keratin protein with another material that may be polymeric or polymer forming.

The invention also describes processes for combining keratin protein with other polymer materials to produce fibres, either before, during or after an extrusion process.

One example the invention refers to a range of processes which may be used to create an intimate mixture of two materials. In one form of this process a solution of keratin proteins, either aqueous or organic solvent based, is combined with a solution containing another material, that may by its nature be a polymer or polymer forming species. These other materials include, but are not restricted to a cellulose derivative, another protein material such as casein, collagen or silk, an alginate or alginate derivative or a synthetic material for example from the acrylic family of polymers or any other synthetic material capable of being solvent spun. This combination of keratin protein with another polymer forming material may occur as a solution of one (for example keratin) is extruded into a solution of another (for example an acrylate solution), provided that the two solutions cause the formation of an insoluble material on combination. Either solution may be extruded into the other. Through this process an intimate mixture of keratin protein and a fibre forming polymer is produced, and a fibrous material formed. The precise nature of the material depends in large part on the nature of the non-keratin component and the spinning conditions. Another process to produce an intimate mixture is one of coextrusion, in which the two components, one containing keratin protein and one other, are mixed immediately prior to extrusion or as extrusion occurs. Extrusion may occur into a solution in which both components are insoluble, or in a dry spinning process in which solvents are removed to leave a fibrous material.

Another example of the invention relates to coextrusion and is one in which keratin is mixed with a synthetic monomer prior to extrusion, and the mixture is extruded into a solution in which the keratin is insoluble, and also contains an initiator to facilitate polymerisation of the monomer thus creating an intimate mixture of keratin protein and a synthetic polymer.

Another example of the invention is a process for coating preformed fibrous materials, such as cotton, cellulose based fibres, acrylic polymer based fibres, nylon, polyester or other common polymers used in fibre production with a keratin protein.

By coating these fibres with keratin protein(s) the properties of those fibres are affected, in particular their handle and comfort characteristics. The fibre surface may be modified to create a favourable interaction between the polymer and the keratin protein by generating charged or polar groups. Methods for achieving this include chemical modification such as oxidation with chlorine or ozone and the use of ionising radiation such as plasma or corona discharge. The keratin protein, which can be applied to the fibre from a solution then forms a strong bond to the fibre surface based on non-covalent interactions and also encirclement of the fibre to form a continuous keratin protein surface. Alternatively, a covalent bond between the fibre and the keratin protein coating may be achieved through the use of treatments that generate suitable reactive groups on the fibre surface. These include the generation of radical species through the use of ionising radiation, and the applications of chemicals specific to the fibre type. In the case of cellulose based fibres, application of periodate will lead to cleavage and oxidation of surface carbohydrate groups with the generation of aldehyde functionality on the fibre surface. This is reactive towards proteins such as keratin protein and thus a covalent bond can be formed between the fibre and the keratin protein coating. The sulphur rich nature of keratin proteins provides a multitude of

reactive sites for the covalent binding of keratin protein to modified fibre surfaces and may be chosen as the target for reactive chemistry. The process of coating fibres with keratin protein may take place after the fibre has been formed, as a surface treatment of cellulose fibres for example, or alternatively as part of a fibre spinning process, for example in the formation of wet spun acrylic fibres.

Another example of the invention describes processes for the formation of graft copolymers between keratin proteins and synthetic monomers, such as those from the vinyl family including, acrylates and styrene-based monomers. As part of the process a polymerisation reaction is initiated between a synthetic monomer and a keratin substance. The keratin substance may be a protein extracted from a protein source, or may be a protein based material present as an insoluble component in a protein source, for example in the form of residues remaining following the extraction of the bulk of the protein from a keratin source. Graft copolymerisation may be promoted by initiating a polymerisation process in the presence of the keratin material. The sulphur containing amino acid residues, prevalent in keratin proteins, may act as an initiating site or as a chain transfer reagent and provide a site for the covalent linkage of the synthetic material to keratin proteins. Composite materials formed in this way may then be further processed, either through dry, wet or melt spinning into fibres, or into other composite polymer materials such as films. The mechanical properties of the synthetic polymer component may be modified by inclusion of suitable comonomers to allow low-temperature thermoforming processes in which the protein component will not be either degraded or, in some cases, denatured from a specific tertiary structure.

Particular examples of the invention have been described and it is envisaged that

improvements and modifications can take place without departing from the scope thereof.

KERATEC LIMITED

By their Attorneys
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